



Fast pyrolysis of torrefied sewage sludge in a fluidized bed reactor



M. Atienza-Martínez^{a,*}, I. Fonts^{a,b}, L. Lázaro^a, J. Ceamanos^a, G. Gea^a

^a Thermochemical Processes Group (GPT), Aragón Institute for Engineering Research (I3A), Universidad de Zaragoza, Edificio I+D, C/Mariano Esquillor s/n, 50018 Zaragoza, Spain

^b Centro Universitario de la Defensa de Zaragoza, Ctra. Huesca s/n, 50090 Zaragoza, Spain

HIGHLIGHTS

- Pyrolysis of dry and torrefied sewage sludge in a fluidized bed reactor was studied.
- The influence of torrefaction conditions on the pyrolysis products was determined.
- The cumulative product yields are not affected by torrefaction.
- Torrefaction step does not improve the liquid homogeneity.
- Torrefaction step does not improve the energy recovery of the organic phases.

ARTICLE INFO

Article history:

Received 4 April 2014

Received in revised form 31 July 2014

Accepted 1 August 2014

Available online 12 August 2014

Keywords:

Torrefaction

Fast pyrolysis

Sewage sludge

Bio-oil

Fluidized bed reactor

ABSTRACT

The pyrolysis of dry and of torrefied sewage sludge in a lab-scale fluidized bed reactor has been studied in order to determine whether torrefaction pre-treatment could enhance the properties of the liquid product obtained after pyrolysis. The aim of this work is to evaluate the influence of the torrefaction temperature (220–320 °C) and average solid residence time (3.6–10.2 min) on the product distribution and the properties of the pyrolysis products. Pyrolysis was conducted at 530 °C with an average solid residence time of 5.7 min and a nitrogen volumetric flow per reactor area of 0.074 m³ (STP) m⁻² s⁻¹ (measured at 0 °C and 1.01·10⁵ Pa). The experimental results show that torrefaction pre-treatment affects the pyrolysis liquid product, although it does not improve the homogeneity of the liquid. Specifically, it reduces the yields of water and the liquid aqueous phase obtained in the pyrolysis step, especially after torrefaction under the most severe conditions, but it does not have a great effect on the properties of the liquid organic phases obtained. The cumulative yields of gas and organic compounds from the two-step process are not different from the yields obtained from one-step pyrolysis.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

As the reserves of fossil fuels are running out and energy consumption is increasing, biomass and wastes are seen as potential sources of energy because they can be converted into fuels and chemicals by means of thermochemical and biochemical processes [1–3], being transformed these raw materials into renewable sources of C and H. Fast pyrolysis of biomass for liquid production is among the most promising of these technologies due to the high yield of bio-oil [4]. Sewage sludge is one of the materials that can be used as feedstock [5]. Pyrolysis is a management technology for sewage sludge that, in addition to reducing its volume, could contribute to obtaining renewable energy and valuable chemicals [5–7].

Sewage sludge pyrolysis liquid is a dark-brown complex mixture of organic compounds and water generated from depolymerization and dehydration reactions [8]. This liquid is not homogeneous and it separates into two or three phases [9–12]. Bio-oil from sewage sludge is rich in water (20–70 mass fraction %), resulting from the moisture in the initial material and from dehydration reactions during pyrolysis [5,13,14]. This high water content lowers the higher heating value and flame temperature of the liquid and causes phase separation, but benefits the viscosity and therefore fluidity [5,8,15]. The oxygen content is higher than in the case of crude oil and its distribution in the different compounds depends on the pyrolysis process conditions and on the raw material. This high oxygen content lowers the energy density of the bio-oil and makes it immiscible with hydrocarbon fuels [8]. Besides, the high oxygen content gives bio-oil a high reactivity during storage, which can cause increased viscosity and phase separation [16].

* Corresponding author. Tel.: +34 876555483; fax: +34 976761879.

E-mail address: atienza@unizar.es (M. Atienza-Martínez).

In order to use bio-oil in turbines or engines as an alternative fuel, it needs to be upgraded due to the drawbacks mentioned above. There are various techniques to improve the fuel properties of bio-oil, either during its production using methods such as *in situ* catalytic cracking of pyrolysis vapours [17–23], or after it is obtained, by means of hydrodeoxygenation (HDO) [24,25] or decarboxylation (DCO) [26]. Integrated catalytic pyrolysis – in a combined pyrolysis–catalysis reaction system – is less flexible in terms of operational conditions since it operates at a single operation temperature and the catalyst has to be robust enough to resist both the temperature and the environment [27]. Besides, some authors have observed that, when using zeolites, the yield of gaseous products and of water increased and therefore the yield of solid product – char – and of organic compounds decreased [28,29]. The improvement of pyrolysis oil by means of its cracking over a catalyst such as zeolite is now under study. There remain some issues to be solved, such as the decrease in the liquid yield, the excessive deoxygenation that could increase the yield of aromatic compounds, and the catalyst deactivation [26]. The disadvantages of HDO are the high hydrogen consumption (reaching values over 700 m³ (STP) per ton of bio oil [30,31]) and the low yield of pyrolysis liquid of high quality (at the best, 0.77 dm³ dm^{−3} oil fed [30]). According to Kersten et al. [26], this process would only make sense as a final step in the deoxygenation process. With DCO, deoxygenation by CO₂ removal can be achieved with the appropriate catalyst, but the removal of oxygen is insufficient [26]. Upgrading by means of emulsification with diesel and biodiesel [32,33] and esterification [34–36] have also been tested with satisfactory results.

The improvement of the liquid can also be achieved by the pre-treatment of the biomass used as feedstock by means of torrefaction [37–39]. Torrefaction (also called roasting or mild pyrolysis [40]) is a thermal treatment which takes place at temperatures between 200 °C and 300 °C under atmospheric pressure conditions and inert atmosphere [40,41]. Torrefaction reduces the oxygen content of lignocellulosic biomass due to the release of water, carbon dioxide, carbon monoxide and lightweight organic compounds [42]. A solid product with lower moisture content and higher energy density is obtained. In the existing literature there are some studies about the effect of torrefaction on the subsequent thermochemical processing of biomass whether through combustion

[41,43–45] or gasification [46–49], but also about torrefaction as pre-treatment for pyrolysis [37,50–56]. In these studies, torrefaction and pyrolysis are normally carried out using fluidized bed reactors or auger reactors. Depending on the torrefaction conditions, liquid from pyrolysis of torrefied biomass has a lower water content and oxygen to carbon ratio [37,55] and higher stability [55,56] and energy content [51,55], but at the expense of a reduction in the liquid yield [37,50,51,53,56]. In view of these results, torrefaction pre-treatment could improve the properties of sewage sludge pyrolysis liquid as a fuel. To the best of our knowledge, torrefaction of sewage sludge as pre-treatment for the improvement of pyrolysis liquid properties has not yet been investigated in detail. Ábrego et al. [57] included torrefaction as one of the steps in a three-stage process aimed at valorizing sewage sludge, but they did not analyze the influence of torrefaction on pyrolysis liquid properties.

This study describes the effect of sewage sludge torrefaction pre-treatment in a fluidized bed reactor (with temperatures between 220 °C and 320 °C and solid residence times between 3.6 min and 10.2 min) on the distribution and the properties of the products obtained after pyrolysis of the torrefied solid. This pyrolysis was also carried out in a fluidized bed reactor. Dry sewage sludge pyrolysis experiments were also carried out for comparison. The goal of the study is to identify whether sewage sludge torrefaction pre-treatment can enhance the fuel properties of pyrolysis liquid.

2. Materials and methods

2.1. Materials

The dry sewage sludge (SS) was provided by a Spanish wastewater treatment plant located in Madrid. The sewage sludge is anaerobically digested and thermally dried in the treatment plant, which generates over 33 kt per year of dry SS. The properties of the dry SS used are listed in Table 1. The bulk density (ρ) was obtained by a non-standardized method. A known volume of dry SS was weighed and the density was calculated. The energy density (ρ_{ener}) results from the multiplication of the density by the higher heating value (HHV). The ash mineral composition of the dry SS, analyzed by Inductively Coupled Plasma-Atomic Emission

Table 1
Properties of dry and torrefied sewage sludge.

	Analytical standard	Units	Dry SS	220/10.2	320/10.2	220/3.6	320/3.6	270/6.1	270/6.1	270/6.1	270/6.1	220/6.1	320/6.1	270/10.2	270/3.6
Carbon	^a	% ^b	29.50	30.75	28.86	29.62	29.94	30.07	28.13	29.32	29.11	29.29	30.28	30.36	29.73
Hydrogen	^a	% ^b	4.67	4.96	3.27	4.90	4.50	4.68	4.50	4.61	4.65	4.71	3.41	4.57	3.95
Nitrogen	^a	% ^b	5.27	5.15	4.71	4.95	5.02	5.18	4.75	4.99	4.83	5.01	5.21	5.14	5.08
Sulfur	^a	% ^b	1.31	1.11	0.61	1.07	1.12	1.01	1.17	1.08	0.94	1.13	0.63	1.03	1.03
Oxygen	^d	% ^b	20.20	16.90	7.83	18.26	15.24	16.30	19.16	18.35	17.57	18.97	8.44	15.82	18.43
O/C	^e		0.37	0.33	0.12	0.31	0.32	0.36	0.40	0.36	0.38	0.38	0.16	0.32	0.35
H/C	^e		1.59	1.76	1.19	1.67	1.66	1.71	1.68	1.65	1.76	1.70	1.29	1.66	1.36
Dry matter	ISO-589-1981	% ^b	93.52	96.2	96.5	93.3	97.2	96.8	95.3	95.1	96.9	95.4	98.8	97.0	95.1
Ash		% ^b	39.04 ^f	41.1 ^g	54.7 ^g	41.2 ^g	44.2 ^g	42.8 ^g	42.3 ^g	41.7 ^g	42.9 ^g	40.9 ^g	53.0 ^g	43.1 ^g	41.8 ^g
HHV ^h	ASTM D-3286-96	MJ kg ^{−1}	12.79	12.90	12.05	13.02	13.62	13.39	13.27	13.23	13.02	13.08	13.25	13.49	13.04
ρ		kg dm ^{−3}	0.862	0.872	0.802	0.880	0.848	0.880	0.878	0.873	0.882	0.862	0.792	0.865	0.873
ρ_{ener}		MJ dm ^{−3}	11.0	11.3	9.7	11.5	11.5	11.8	11.6	11.5	11.5	11.3	10.6	11.7	11.4

^a Ultimate analysis was performed using Carlo Erba 1108.

^b Mass fraction %.

^c The % of hydrogen includes the hydrogen from moisture.

^d Oxygen (%) = 100 – carbon (%) – hydrogen (%) – nitrogen (%) – sulfur (%) – ash (%).

^e Molar basis; without moisture O and H.

^f The % of ash in the dry SS was determined according to ISO-1171-1976.

^g The % of ash in the TSS was determined taking into account the yield to TSS and the ash content of the raw SS: $\text{ash}_{\text{TSS}} (\%) = 100 \cdot \frac{\text{ash}_{\text{SS}} (\%)}{\eta_{\text{TSS}} (\%)}$.

^h HHV was determined using IKA C 2000 Basic Calorimeter.

Spectroscopy (ICP-AES), has been shown elsewhere [57]. This dry sewage sludge is rich in iron and silica. The different types of torrefied sewage sludge (TSS) used in this study were obtained in a previous work [39]. Torrefaction was carried out in a laboratory scale fluidized bed reactor under different temperatures and solid residence times. The torrefaction temperature was set to 220 °C, 270 °C and 320 °C and the average solid residence time was 3.6 min, 6.1 min and 10.2 min. The dry SS particle size was in the range of 250–500 µm. The properties of TSS used in this work are also listed in Table 1. Torrefied sewage sludge samples are named x/y, where x is the torrefaction temperature and y is the torrefaction solid residence time. The ash content of the torrefied SS was calculated taking into account the ash content of the dry SS and the yield of torrefied solid.

2.2. Experimental system and procedure

Two processes have been analyzed in this study: fast pyrolysis of dry sewage sludge and fast pyrolysis of torrefied sewage sludge. A scheme of these processes is shown in Fig. 1a (fast pyrolysis of dry SS) and Fig. 1b (fast pyrolysis of TSS).

2.2.1. Pyrolysis tests

A lab-scale fluidized bed reactor (<1 kg h⁻¹) was used to perform fast pyrolysis experiments. The same reactor was used previously to prepare the TSS samples [39]. Fluidized bed reactors provide high heating rates. The experimental plant consisted of a screw feeder, a fluidized bed reactor, a condensation system for the liquid collection and a gas analysis system. The schematic of the experimental plant as well as the experimental procedure carried out during the pyrolysis have been shown elsewhere [58].

Fast pyrolysis operational conditions were kept constant for all the experiments to study the effect of the torrefaction on fast pyrolysis products and their properties. The average run time was 75 min. The solid residence time was calculated as the ratio between the mass of char remaining in the bed after the experiment and the flow of TSS (or dry SS) fed during the experiment. The average solid residence time for fast pyrolysis experiments was 5.7 min. The nitrogen volumetric flow per reactor area was 0.074 m³ (STP) m⁻² s⁻¹ (ratio between the fluidization velocity and the minimum fluidization velocity of the bed around 8). Average gas residence time was around 3 s, calculated as the ratio between the volume of the reactor (bed volume plus freeboard volume) and the volumetric flow of flue non-condensable gases (NCG) at 530 °C.

2.2.2. Pyrolysis product analyses

The mass yields of each one of the TSS pyrolysis products were calculated as the percentage ratio between the mass of pyrolysis product ($m_{\text{pyrolysis product}}$) obtained and the mass of dry SS introduced in the torrefaction process ($m_{\text{dry SS fed}}$) (or during pyrolysis in the case of fast pyrolysis of dry SS), using Eq. (1):

$$\eta_{\text{product}} (\%) = \left(\frac{m_{\text{pyrolysis product}}}{m_{\text{dry SS fed}}} \right) \times 100 \quad (1)$$

The mass of char obtained was determined by difference in weight of the vessels in which it was collected. For each experiment, the bulk density (ρ_{char}) and the higher heating value (HHV_{char}) of char were determined three times with the same methods used for the dry SS. The specific surface area (S_{BET}) was determined following the Brunauer–Emmet–Teller (BET) method using a Micromeritics TriStar 3000 gas adsorption analyzer.

The mass of NCG obtained from pyrolysis was calculated taking into account the gas composition provided by the micro-gas chromatograph (micro-GC; Agilent 3000A) analysis and the known volumetric flow of nitrogen introduced. The lower heating value of the gas (LHV_{gas}) was calculated taking into account the composition of the gas and the higher heating value of each compound.

The mass of liquid obtained was calculated by difference in weight of the devices in which it condensed. The liquid was stored in a fridge at 3–5 °C until it was analyzed. For a proper characterization of each phase, the liquid was centrifuged at 4500 rpm (2038×g) during 30 min using an Heraeus Megafuge 16 Centrifuge and the different phases were separately collected. The liquid separated into three different phases: light organic phase (LOP), heavy organic phase (HOP) and aqueous phase (AP). The distribution of the compounds in the different phases is related to the polarity and to the density of the compounds. The water content (mass fraction %) of the different phases (W_{phase}) was quantified by the Karl-Fischer titration method (Mettler Toledo V-20 analyzer) using appropriate Karl-Fisher reagents for samples that contain aldehydes and ketones. The density (ρ_{phase}) of the HOP and the AP was determined using a portable Mettler Toledo densimeter (model Densito 30 PX). The density of the LOP was determined by weighing a known volume using a microsyringe, due to the small amounts obtained. The yield of each one of the phases (η_{phase}) was calculated using the whole liquid yield, and the volumetric distribution and the density of each phase. For the organic phases, the higher heating value ($\text{HHV}_{\text{phase}}$) and the energy recovery ($\eta_{\text{energy,phase}}$) were also determined. The energy recovery

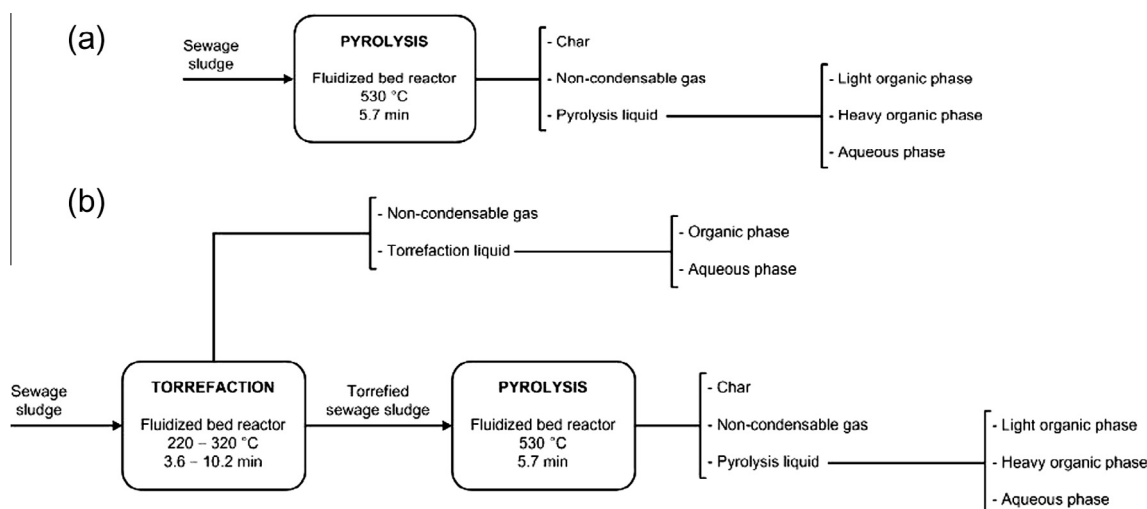


Fig. 1. Flowsheets of the processes carried out. (a) Pyrolysis of raw sewage sludge (b) Pyrolysis of torrefied sewage sludge.

indicates the energy content of dry SS contained in the phase. This is calculated using Eq. (2):

$$\eta_{\text{energy,phase,i}} (\%) = \frac{\eta_{\text{phase,i}} \cdot \text{HHV}_{\text{phase,i}}}{\text{HHV}_{\text{dry SS}}} \quad (2)$$

where $\eta_{\text{phase,i}}$ is the yield of the liquid phase, $\text{HHV}_{\text{phase,i}}$ is the higher heating value of the liquid phase and $\text{HHV}_{\text{dry SS}}$ is the higher heating value of dry SS. The dynamic viscosity of the HOP (μ_{HOP}) was determined at room temperature using a Fungilab rotational viscometer (Visco Basic Plus). The content of ammoniacal nitrogen ($\text{NH}_3\text{-N}$) in the AP was determined taking into account the APHA standards [59]. The yield of ammoniacal nitrogen ($\eta_{\text{NH}_3\text{-N}}$) was calculated using the yield of the AP and the content of ammoniacal nitrogen in the AP.

The water content of the liquid (W_{liquid}) was calculated using the yield of each phase and their water contents. The total water content together with the liquid yield allowed the calculation of the yield of water (η_{water}). The yield of organic compounds (η_{organic}) was calculated as the difference between the liquid and the water yields.

The identification and semi quantification of the organic compounds present in the three phases of the liquid were performed by gas chromatography using an Agilent 7890A GC chromatograph with an Agilent 5975C mass selective detector (MSD) and a flame ionization detector (FID). The samples were dissolved in the appropriate solvents and were derivatized with N,O-Bis(trimethylsilyl)trifluoroacetamide with trimethylchlorosilane when necessary. The area percentage of the integration peaks of the identified compounds was used for the comparison of the chemical composition.

2.3. Experimental design

A Full Factorial Design (FFD) was used to study the influence of the torrefaction operational conditions and their interactions on the fast pyrolysis products, especially on the properties of the liquid product. Factorial designs are suitable for studying the effect of the experimental variables and their interactions [38,56]. The factors evaluated were the torrefaction temperature, T_{torr} (220–320 °C), and the torrefaction solid feed rate, $Q_{\text{feed,torr}}$ (6–16 g min^{−1}) (4 runs). The solid feed rate was chosen as one of the factors instead of the solid residence time to ensure that the two factors were independent [39]. The different solid feed rates corresponded to different torrefaction solid residence times (t_{torr}) (10.2–3.6 min). 4 replicas at the center point conditions – 270 °C and 11 g min^{−1} (6.1 min) – were carried out to evaluate the experimental error and the curvature of the evolution of the response variables [60]. The response variables studied are specified in Table 2. The experimental data were analyzed through analysis of variance (ANOVA) with a confidence level of 95%. If the evolution of the response variable is not linear, it will be necessary to carry out more experiments under different conditions to determine which factor causes the curvature. The ANOVA analyses revealed that some response variables of the present study did not show a linear trend, and thus the experimental design was augmented with 4 axial runs. Therefore, 12 fast pyrolysis runs were performed using TSS as feedstock.

The Face Centered Central Composite Design (FCCCD) used allows the fitting of second-order models if the response variables do not follow a linear trend with the factors within the range of study [60]. The model coefficients allow the determination of the

Table 2
Response variables studied.

Product	Variable	Nomenclature	Units
Char	Char yield	η_{char}	% ^a
	Higher heating value (daf)	$\text{HHV}_{\text{char}} (\text{daf})$	MJ kg ^{−1}
	BET specific surface area	S_{BET}	m ² g ^{−1}
Liquid	Liquid yield	$\eta_{\text{liq,pyr}}$	% ^a
	LOP yield	η_{LOP}	% ^a
	LOP water content	W_{LOP}	% ^a
	LOP higher heating value	HHV_{LOP}	MJ kg ^{−1}
	LOP energy recovery	$\eta_{\text{energy,LOP}}$	%
	Chemical composition of the LOP		
	HOP yield	η_{HOP}	% ^a
	HOP water content	W_{HOP}	% ^a
	HOP higher heating value	HHV_{HOP}	MJ kg ^{−1}
	HOP energy recovery	$\eta_{\text{energy,HOP}}$	%
	HOP viscosity	μ_{HOP}	mPa s
	Chemical composition of the HOP		
	AP yield	η_{AP}	% ^a
	AP water content	W_{AP}	% ^a
	NH ₃ -N yield	$\eta_{\text{NH}_3\text{-N}}$	% ^a
	Chemical composition of the AP		
	Water yield	η_{water}	% ^a
	Liquid water content	W_{liquid}	% ^a
	Organic compounds yield	η_{organic}	% ^a
Gas	Permanent gases yield	$\eta_{\text{gas,pyr}}$	% ^a
	CO ₂ yield	η_{CO_2}	% ^a
	H ₂ S yield	$\eta_{\text{H}_2\text{S}}$	% ^a
	C ₂ H ₄ yield	$\eta_{\text{C}_2\text{H}_4}$	% ^a
	C ₂ H ₆ yield	$\eta_{\text{C}_2\text{H}_6}$	% ^a
	H ₂ yield	η_{H_2}	% ^a
	CH ₄ yield	η_{CH_4}	% ^a
	CO yield	η_{CO}	% ^a
	Gas lower heating value	LHV_{gas}	MJ m ^{−3} (SPT)
	Cumulative gas yield	$\eta_{\text{gas,cum}}$	% ^a
	Cumulative liquid yield	$\eta_{\text{liq,cum}}$	% ^a
Torrefaction + pyrolysis	Cumulative water yield	$\eta_{\text{water,cum}}$	% ^a
	Cumulative organic compounds yield	$\eta_{\text{organic,cum}}$	% ^a

^a Mass fraction.

relative influence of each factor on one variable. The higher the coefficient, the higher is the factor effect. To study the influence of torrefaction conditions, both the plots represented and the discussion of the results are based on the values calculated from the models.

For the comparison of the results from dry SS pyrolysis with the results from TSS pyrolysis, 2 additional fast pyrolysis runs using dry SS as feedstock were performed. In this case, only one factor was investigated. Therefore, one-way analysis of variance (one-way ANOVA), at a confidence level of 95%, was applied to determine whether torrefaction pre-treatment has effect on the pyrolysis products and their properties or not [60]. When a significant effect of torrefaction was detected by one-way ANOVA analysis, a multiple range test – Fisher's LSD test – was used to compare pairs of values and determine which torrefaction conditions cause differences in pyrolysis product yields and properties compared to pyrolysis of dry SS.

3. Results and discussion

3.1. Pyrolysis product yields

The mass yields of each of the fast pyrolysis products obtained (char, liquid and NCG) are expressed in mass of feedstock. Mass balance closures are over 94% (Table 3), taking into account both the torrefaction and fast pyrolysis processes or only pyrolysis when dry sewage sludge is used directly as feed (Table 3). The yield of torrefied solid obtained under the different torrefaction conditions studied can be found elsewhere [39]. In all cases, the char is the major product while the gas is the minor product. Only the yield of the liquid product obtained in the pyrolysis step is affected by torrefaction pre-treatment of sewage sludge. Other authors have also found that the yield of pyrolysis char from other types of biomass was not affected by this pre-treatment at torrefaction temperatures lower than 290 °C and a solid residence time of 25 min [52].

The fast pyrolysis liquid yield ($\eta_{\text{liq,pyr}}$) varies between $12 \pm 3\%$ and $34 \pm 3\%$ within the range of study (Fig. 2a). The torrefaction temperature is the most influential parameter on the pyrolysis liquid product yield (the highest model coefficient, as can be observed in Table 4). As the interaction between the torrefaction temperature and the solid residence time is significant, the effect of the torrefaction temperature depends on the value of the solid residence time. At solid residence times of 6.1 min or longer, the

liquid yield decreases if the temperature is above 270 °C, while at the shortest solid residence times the temperature does not have a great effect on the pyrolysis liquid yield. During torrefaction most of the devolatilization reactions take place at temperatures higher than 270 °C and solid residence times longer than 6.1 min, within the studied intervals. At these severe conditions, dry SS reacted to a greater extent during the torrefaction process, producing a significant water loss (with yields of water from torrefaction higher than the initial moisture content of dry SS) and some organic compound release (yields of organic compounds from torrefaction over 5%) [39]. Therefore, there are fewer sewage sludge compounds which can undergo chemical reactions during the pyrolysis stage. If torrefaction is carried out at 320 °C, the pyrolysis liquid yield decreases from $26 \pm 3\%$ to $12 \pm 3\%$ while increasing the solid residence time during torrefaction from 3.6 min to 10.2 min. These results are consistent with those obtained by Meng et al. for loblolly pine chips [37] and by Boateng et al. for hardwood and switchgrass [55]. Liaw and co-workers observed that torrefaction temperatures higher than 270 °C in an auger reactor provoke a decrease in the yield of liquid from pyrolysis of torrefied fir wood, even at a torrefaction solid residence time of 72 s [53]. The decrease in liquid yield may be the result of the devolatilization of the dry SS during torrefaction, as other authors such as Zheng et al. have mentioned [50].

The liquid yield obtained using SS torrefied at 320 °C as feedstock for pyrolysis, whatever the solid residence time, is lower than the pyrolysis liquid yield obtained using dry SS (Fig. 2b). Therefore, torrefaction at high temperatures provokes a decrease in the pyrolysis liquid yield because of the decomposition suffered by the sewage sludge during torrefaction. The liquid yield obtained using SS torrefied at 10.2 min, whatever the torrefaction temperature, is lower than the pyrolysis liquid yield obtained using dry SS (Fig. 2b). Then, torrefaction at long solid residence times also provokes a decrease in the pyrolysis liquid yield.

There are no significant differences between the cumulative liquid yield ($\eta_{\text{liq,cum}}$), calculated as the sum of the torrefaction liquid yield and the pyrolysis liquid yield, obtained at the different torrefaction conditions and the liquid yield obtained from pyrolysis of dry SS, as can be observed in Fig. 2c. Although the pyrolysis liquid yield is affected by torrefaction operational conditions, the sum of the liquid yields obtained from the two processes – torrefaction and pyrolysis – is not affected by these operational conditions. In the same way, the cumulated yield of the gas product ($\eta_{\text{gas,cum}}$), from both torrefaction and pyrolysis steps is not affected

Table 3
Design matrix, yields to pyrolysis products and to torrefaction liquid and NCG, and mass balance.

	Average torrefaction solid residence time (min)								
	3.6	6.1	10.2	3.6	6.1	10.2	3.6	6.1	10.2
T_{torr} (°C)	Torrefaction residence time (min)			η_{char} (%)			$\eta_{\text{liq,pyr}}$ (%)		
220	3.6	6.3	10.8	46	48	51	32	35	31
270	4.1	6.4 ± 0.3^a	9.1	46	49 ± 1^a	47	34	32 ± 1^a	31
320	3.0	4.6	10.7	48	48	49	27	17	13
Dry SS ^b	-				49 ± 1			37 ± 1	
Coefficient of variation ^c (%)		5			2			3	
T_{torr} (°C)	$\eta_{\text{liq,torr}}$ (%)			$\eta_{\text{gas,torr}}$ (%)			Mass balance (%)		
220	7.6	4.4	6.6	0.02 ^d	0.03 ^d	0.09	95	97	98
270	5.6	7.0 ± 0.9^a	8.2	0.06	0.14 ± 0.03^a	0.23	96	98 ± 3^a	95
320	9.7	21.6	22.7	0.57	2.94	2.73	95	96	94
Dry SS ^b		-			-			95 ± 2	
Coefficient of variation ^c (%)		13			21			3	

^a Mean value \pm standard deviation. Calculated from the results obtained for the different response variables at the center point conditions.

^b Dry sewage sludge pyrolysis. Mean value \pm standard deviation.

^c Calculated from the results obtained for the different response variables at the center point conditions. Calculated taking into account the mean value and the standard deviation: Coefficient of variation (%) = $100 \cdot \frac{\text{Mean value}}{\text{Standard deviation}}$.

^d Under detection precision.

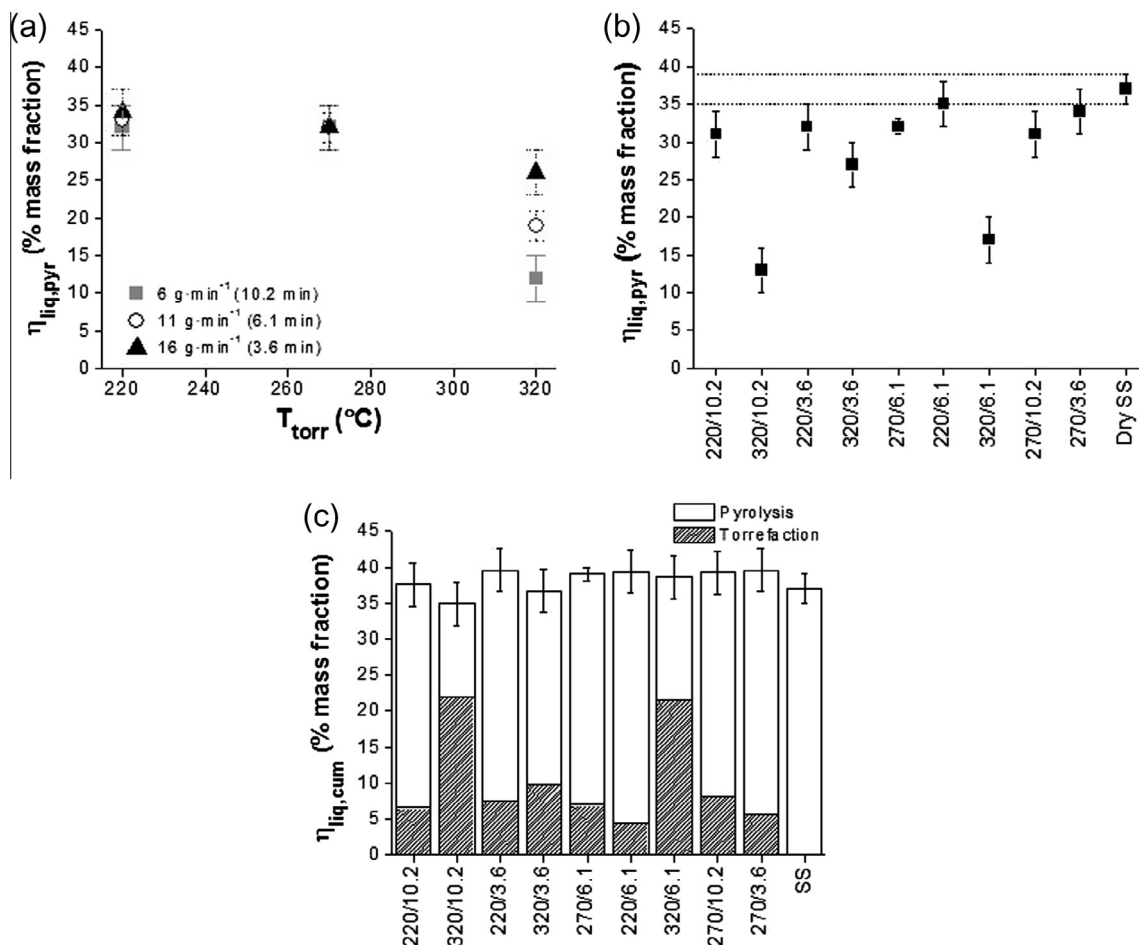


Fig. 2. (a) Pyrolysis liquid yield vs. torrefaction temperature for different torrefaction solid feed rate values. The results are expressed as the model value at each torrefaction condition ± 0.5 Fisher LSD interval (taking into account all the runs). (b) Comparison of SS pyrolysis liquid yield and TSS pyrolysis liquid yield (LSD interval). (c) Comparison of the sum of liquid yields obtained from the two processes and SS pyrolysis liquid yield (LSD interval).

Table 4

Coefficients of the terms of the coded model of the factorial design for the response variables. Mean value ± 0.5 Confidence interval (95%).

	Response variable	Independent term	T	Q_{feed}	$T \cdot Q_{feed}$	T^2	Q_{feed}^2	$T^2 \cdot Q_{feed}$	$T \cdot Q_{feed}^2$	$R^{2a,b}$
Product distribution	η_{liq} (%)	32 ± 2	-7 ± 2	n.s. ^c	3 ± 2	-6 ± 3	n.s. ^c	4 ± 2	n.s. ^c	0.95
	η_{water} (%)	13.6 ± 0.9	-5.6 ± 1.4	1.7 ± 0.8	1.2 ± 1.0	-3.9 ± 1.2	1.5 ± 1.2	n.s. ^c	2.1 ± 1.7	0.99
	$\eta_{organic}$ (%)	19 ± 1	-3 ± 1	n.s. ^c	2 ± 1	-3 ± 2	-2 ± 2	2 ± 1	n.s. ^c	0.96
Liquid	η_{LOP} (%)	3.0 ± 0.3	-0.4 ± 0.3	n.s. ^c	0.5 ± 0.4	-0.6 ± 0.5	-0.6 ± 0.5	n.s. ^c	n.s. ^c	0.89
	$\eta_{energy,LOP}$ (%)	10 ± 1	-1 ± 1	n.s. ^c	2 ± 1	-2 ± 2	-2 ± 2	n.s. ^c	n.s. ^c	0.89
	η_{AP} (%)	18 ± 2	-5 ± 2	n.s. ^c	n.s. ^c	-4 ± 3	n.s. ^c	3 ± 2	n.s. ^c	0.89
	η_{NH3-N} (%)	0.64 ± 0.07	-0.15 ± 0.07	0.11 ± 0.07	0.10 ± 0.07					0.99

^a Coefficient of determination, defined as the ratio between the sum of squares explained by the model and the total sum of squares.

^b Lack of fit not significant (p -value > 0.05).

^c Not significant term (p -value > 0.05).

by the application of a previous torrefaction step neither by the different operational conditions used in this stage. Lastly, the yields of char (η_{char}) obtained are not significantly different when this product is generated in a single pyrolysis step using dry SS or when it results from the combination of both, torrefaction and pyrolysis, regardless of the operational conditions used in torrefaction (Table 3). Liaw et al. observed that torrefaction of fir wood at temperatures lower than 330 °C does not affect the cumulative yield of char, liquid and NCG [53]. Ren and co-workers also observed that the total liquid yield from both torrefaction and pyrolysis was similar to the liquid yield from pyrolysis when using fir pellets [56]. Westerhof et al. claim that, for pine wood, if the cumulative yield

from the two-step process and the yield from one-step pyrolysis are not different, the reactions that take place and the changes undergone by the raw material during torrefaction at temperatures of 260 °C and 290 °C and a solid residence time of 25 min do not significantly affect fast pyrolysis at between 450 °C and 550 °C [52].

Pyrolysis liquid is a mixture of water and organic compounds. The analysis of the yield of water and the yield of organic compounds is useful for checking whether torrefaction pre-treatment affects the amounts of these products, even though the cumulative liquid yield is not affected by this pre-treatment.

The water yield obtained in the pyrolysis of torrefied SS varies between $4.1 \pm 1.2\%$ and $16.8 \pm 1.3\%$ (Fig. 3a). The water yield

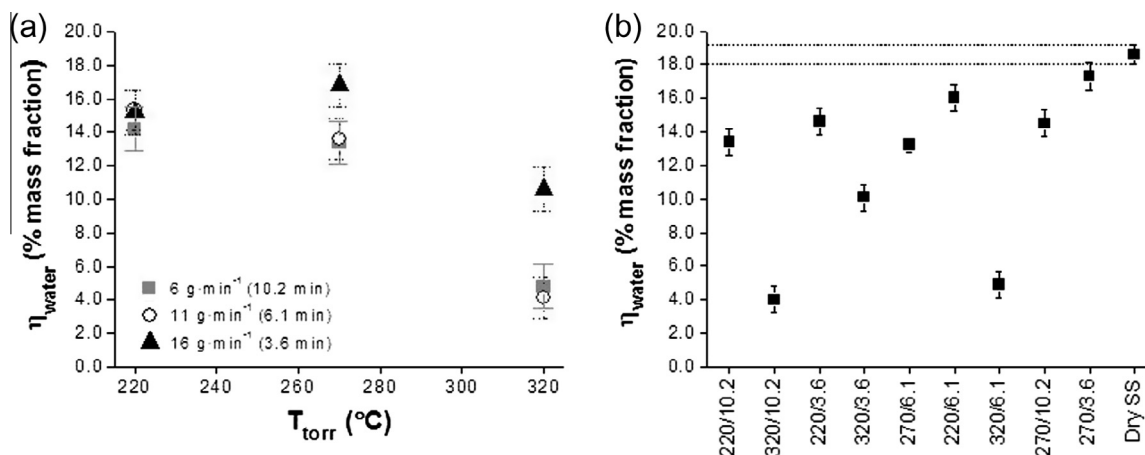


Fig. 3. (a) Water yield vs. torrefaction temperature for different torrefaction solid feed rate values. The results are expressed as the model value at each torrefaction condition ± 0.5 -Fisher LSD interval (taking into account all the runs). (b) Comparison of SS pyrolysis water yield and TSS pyrolysis water yield (LSD interval).

decreases as the torrefaction temperature increases from 270 °C to 320 °C at all the solid residence times studied. An increase in torrefaction solid residence time from 3.6 min to 6.1 min provokes a decrease in the water yield at torrefaction temperatures equal or higher to 270 °C. At torrefaction temperatures of 320 °C and solid residence times longer than 6.1 min, dehydration reactions begin to be significant during torrefaction.

Non-torrefied SS achieves the highest water yield, as can be observed in Fig. 3b. The decrease in water yield caused by torrefaction is more pronounced when SS torrefied at 320 °C is used as feedstock for pyrolysis, because it has lost a great amount of water during torrefaction.

Depending on the torrefaction parameters, the yield of organic compounds after pyrolysis varies between $7 \pm 2\%$ and $19 \pm 1\%$ (Fig. 4a). The yield of organic compounds decreases with increasing the torrefaction temperature from 270 °C to 320 °C, at solid residence times equal to or longer than 6.1 min. Liaw et al. observed that the yield of organic compounds from pyrolysis of torrefied fir wood started to decrease at torrefaction temperatures higher than 270 °C [53]. The organic compounds yield is lower when increasing solid residence time from 3.6 min to 10.2 min at 320 °C (Fig. 4a). The presence of organic compounds in torrefaction liquid was only noticeable when torrefaction was carried out at severe conditions (320 °C and solid residence times equal or longer than 6.1 min) reaching values over 7% [39]. This is reflected in the

decrease in the organic compounds yield in the pyrolysis of these torrefied solids.

TSS torrefied at severe conditions (320 °C and solid residence time longer than 6.1 min) used as feedstock for pyrolysis yields lower organic compounds than dry SS (Fig. 4b). Therefore, it seems clear that the reduction in the organic compounds yield in pyrolysis compared to the pyrolysis of dry SS is mainly due to the organic compound loss during torrefaction at these conditions.

There can be no assurance that the yield of organic compounds obtained from pyrolysis of dry SS is different from the yield of organic compounds obtained from the whole process ($\eta_{\text{org,cum}}$, calculated as the sum of the yields of torrefaction organic compounds and of pyrolysis organic compounds).

3.2. Char properties

It cannot be assured that the higher heating value (daf) (HHV_{char} (daf)) of char from TSS pyrolysis is different from this parameter of char from dry SS pyrolysis (Table 5).

Due to the limitations of the technique in this range (between $15 \text{ m}^2 \text{ g}^{-1}$ and $18 \text{ m}^2 \text{ g}^{-1}$), the effect of torrefaction on the BET specific surface area (S_{BET}) of char is not statistical analyzed here. The tentative values obtained give an idea of the low specific area of char from dry SS and TSS pyrolysis.

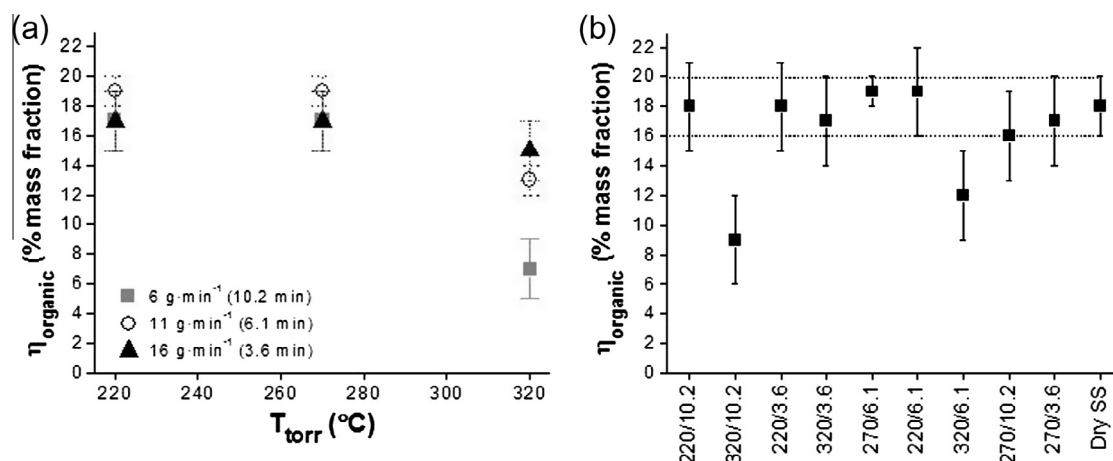


Fig. 4. (a) Organic compounds yield vs. torrefaction temperature for different torrefaction solid feed rate values. The results are expressed as the model value at each torrefaction condition ± 0.5 -Fisher LSD interval (taking into account all the runs). (b) Comparison of SS pyrolysis organic compounds yield and TSS pyrolysis organic compounds yield (LSD interval).

Table 5

Experimental results obtained for the response variables non-significantly influenced by the torrefaction pre-treatment.

	Average torrefaction solid residence time (min)								
	3.6	6.1	10.2	3.6	6.1	10.2	3.6	6.1	10.2
T_{torr} (°C)	$\eta_{\text{gas,cum}}$ (%)			$\eta_{\text{liq,cum}}$ (%)			$\eta_{\text{water,cum}}$ (%)		
220	9	10	9	40	39	38	21.7	20.1	19.6
270	10	10 ± 2 ^a	9	40	39 ± 1 ^a	39	22.6	19.8 ± 0.5 ^a	22.6
320	11	9	10	37	39	35	19.8	20.1	19.2
Dry SS ^b	–			–			–		
Coefficient of variation ^c (%)	20			3			5		
T_{torr} (°C)	HHV _{char} (daf) (MJ kg ^{−1})			η_{CO_2} (%)			η_{CO} (%)		
220	25	30	26	7	7	7	1.1	1.3	1.2
270	28	27 ± 1 ^a	26	8	7 ± 1 ^a	7	1.3	1.4 ± 0.2 ^a	1.2
320	25	29	26	7	5	5	1.6	1.0	1.0
Dry SS ^b	31 ± 4			8 ± 1			1.3 ± 0.1		
Coefficient of variation ^c (%)	4			14			14		
T_{torr} (°C)	$\eta_{\text{C}_2\text{H}_6}$ (%)			η_{H_2} (%)			η_{CH_4} (%)		
220	0.11	0.14	0.12	0.13	0.15	0.14	0.31	0.36	0.34
270	0.14	0.14 ± 0.02 ^a	0.13	0.14	0.18 ± 0.04 ^a	0.14	0.38	0.40 ± 0.08 ^a	0.36
320	0.17	0.13	0.12	0.20	0.11	0.14	0.46	0.31	0.35
Dry SS ^b	0.14 ± 0.01			0.17 ± 0.03			0.38 ± 0.04		
Coefficient of variation ^c (%)	14			22			20		
T_{torr} (°C)	LHV _{gas} (MJ m ^{−3} (SPT))			W_{liquid} (%)			W_{LOP} (%)		
220	8.2	8.4	8.4	45	46	43	1.3	1.2	<1 ^d
270	8.3	8.8 ± 0.4 ^a	8.8	51	41 ± 1 ^a	47	2.0	1.3 ± 0.4 ^a	1.2
320	9.4	9.9	10.1	38	29	30	<1 ^d	1.1	1.6
Dry SS ^b	8.4 ± 0.1			51 ± 2			<1 ^d		
Coefficient of variation ^c (%)	5			2			31		
T_{torr} (°C)	$\eta_{\text{energy,LOP}}$ (%)			η_{HOP} (%)			W_{HOP} (%)		
220	6	10	8	11.9	12.0	11.7	9	7	7
270	8	10 ± 1 ^a	7	10.9	12.6 ± 0.9 ^a	10.3	12	10 ± 2 ^a	8
320	8	6	3	11.3	8.7	8.0	8	6	7
Dry SS ^b	9 ^e			10.0 ± 0.3			9 ± 1		
Coefficient of variation ^c (%)	10			7			20		
T_{torr} (°C)	μ_{HOP} (mPa s)			W_{AP} (%)			HHV _{HOP} (MJ kg ^{−1})		
220	180	258	319	72	75	73	31	33	32
270	287	286 ± 200 ^a	216	78	71 ± 1 ^a	73	29	31 ± 3 ^a	32
320	242	216	115	71	66	78	32	32	33
Dry SS ^b	297 ± 100			75 ± 4			30 ± 1		
Coefficient of variation ^c (%)	70			1			10		

^a Mean value ± standard deviation. Calculated from the results obtained for the different response variables at the center point conditions.^b Dry sewage sludge pyrolysis. Mean value ± standard deviation.^c Calculated from the results obtained for the different response variables at the center point conditions. Calculated taking into account the mean value and the standard deviation: Coefficient of variation (%) = $100 \cdot \frac{\text{Mean value}}{\text{Standard deviation}}$.^d Under detection precision.^e Only one replicate.

3.3. Gas properties

Neither the application of a previous torrefaction step, nor the operational conditions used in torrefaction affect on the yield of any of the gases present in the gas stream obtained from pyrolysis. Carbon dioxide is the major component in both pyrolysis of dry SS and TSS. As expected from the composition results, the LHV_{gas} (N₂ free) is not affected by this pre-treatment (Table 5).

3.4. Liquid properties

As mentioned above, the pyrolysis liquid separated into three phases, regardless of whether or not torrefaction pre-treatment was carried out. There was a minority fluid organic phase on the top, called light organic phase (LOP), which was rich in hydrocarbons and therefore, with an elevated higher calorific value. A viscous organic phase, here namely heavy organic phase (HOP), which is rich in oxygenated compounds and appeared in the middle of the liquid sample. The aqueous phase (AP) placed in the bottom had by far the highest water content. These three phases appeared in previous works [12,61]. Although the liquid water

content (W_{liquid}) is reduced with torrefaction by as much as 43% reaching values of 29% (Table 5) the liquid still separates into three phases. A massive reduction in the water content of the pyrolysis liquid is not enough to achieve liquid homogeneity, as has been reported before by Gil-Laguna et al. [61]. The decrease in W_{liquid} with torrefaction severity is due to the increase in the water released through drying and dehydration reactions during torrefaction.

The effect of torrefaction on the properties of the liquid phases affected by this pre-treatment is analyzed below.

3.4.1. LOP

No significant differences in terms of water content and higher heating value of the LOP obtained from the different experiments can be noted (Table 5). Only the yield of the LOP, the energy recovery and the chemical composition of this phase are affected by torrefaction.

3.4.1.1. LOP yield. The LOP yield varies between $0.9 \pm 0.4\%$ and $3.0 \pm 0.4\%$ (Fig. 5). The torrefaction temperature affects the LOP yield at solid residence times longer than 6.1 min (LOP yield

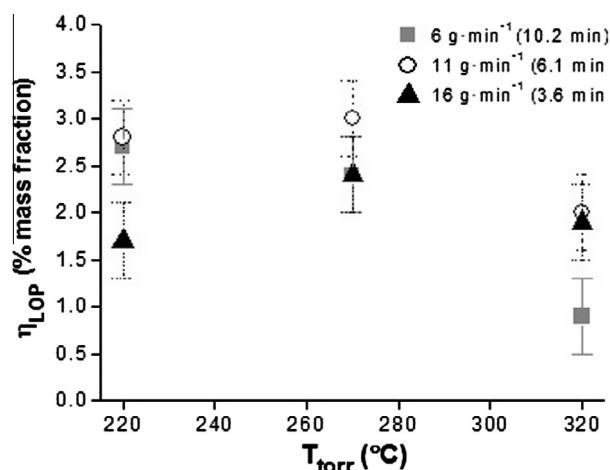


Fig. 5. LOP yield vs. torrefaction temperature for different torrefaction solid feed rate values. The results are expressed as the model value at each torrefaction condition ± 0.5 -Fisher LSD interval (taking into account all the runs).

decreasing from 270 °C to 320 °C). The solid residence time has a significant effect on the yield of the LOP when the pre-treatment is carried out at 320 °C. At this temperature the yield of LOP is lower when the solid has been torrefied at the longest solid residence time in this study (10.2 min).

3.4.1.2. Energy recovery of the LOP. Since the HHV_{LOP} is not affected by torrefaction, the variation in $\eta_{energy,LOP}$ is caused by the variation in the LOP yield. This parameter ranges from $3 \pm 1\%$ to $10 \pm 1\%$ within the range of study. The observed trends in the energy recovery of the LOP are the same as those observed in the yield of this phase.

When comparing pyrolysis of TSS with pyrolysis of dry SS (LOP energy recovery of 9%), only the energy recovery of the LOP obtained from SS torrefied at the most severe conditions (320 °C and 10.2 min) is significantly lower (Table 5). The sewage sludge suffered the greatest loss of organic compounds such as steroids and their derivatives during torrefaction at these conditions [39].

3.4.1.3. Chemical composition of the LOP. GC–MS analyses were carried out to know the LOP composition. The organic compounds identified in the LOP obtained from pyrolysis of dry SS, TSS at 220 °C and 10.2 min and TSS at 320 °C and 6.1 min have been grouped into chemical families. The organic compounds whose area percentage is larger than 1% are listed in Table 6. The area percentage of each one of the chemical families is shown in Fig. 6. The three light organic phases analyzed are rich in steroids and their derivatives such as (5 α)-cholest-3-ene, cholest-4-ene, cholesta-2,4-diene and (3 β)-cholest-5-en-3-ol. These compounds come from the devolatilization of the extractives present in dry SS [62]. The decline in the proportion of steroids and their derivatives after torrefaction at severe conditions could be related to the loss of extractive compounds during torrefaction since these compounds are abundant in the organic phase obtained in torrefaction of dry SS at a temperature of 320 °C and a solid residence time of 6.1 min [39]. The aliphatic hydrocarbons present in the LOP (1-hexadecene and octadecane, among others) could be originated from the devolatilization of the alkanes and alkenes present in the dry sewage sludge [62] and also from the pyrolysis of other constituents such as carboxylic acids [63], triglycerides [64,65] and steroids [66]. As some of the oxygen-containing aliphatic compounds (mainly fatty acids and fatty alcohols) present in this phase were also present in the extractives of the dry sewage sludge, it

seems that they could come from the devolatilization of sewage sludge [62].

3.4.2. HOP

Neither the yield nor the water content and the higher heating value of the HOP are affected by torrefaction within the range of study. Besides, the energy recovery of this phase (calculated by Eq. (2)) is not improved by torrefaction (Table 5). At the torrefaction temperatures studied, maybe longer solid residence times are required to provoke changes in the properties of the HOP. The HOP behaves as a pseudoplastic and its viscosity depends on the shear rate (varied between 0.3 s^{-1} and 93 s^{-1}). The values obtained at the highest shear rate have been compared and it is not possible to observe the effect of the torrefaction step on the viscosity of this phase due to the high measurement errors. In any case, the values of viscosity obtained are too high to use this phase as a fuel (Table 5).

3.4.2.1. Chemical composition of the HOP. The organic compounds identified in the HOP obtained from pyrolysis of dry SS, TSS at 220 °C and 10.2 min and TSS at 320 °C and 6.1 min have been grouped into chemical families (see Fig. 7). The organic compounds whose area percentage is larger than 1% are listed in Table 6. Other authors have mentioned that the proportion of ash in the material fed could cause differences in the chemical composition, since ash can act as a catalyst [62,67]. The decrease in the proportion of oxygen-containing aliphatic compounds (mainly fatty acids, such as palmitic acid and stearic acid) and steroids and their derivatives such as cholest-2-ene and (5 β)-cholest-3-ene with the torrefaction pre-treatment is appreciable. Oxygen-containing aliphatic compounds are present in torrefaction liquid since they are generated at low temperatures. These are the main organic compounds in the organic phase obtained in torrefaction of dry SS at a temperature of 320 °C and a solid residence time of 6.1 min [39]. Therefore, the proportion of these compounds in the pyrolysis HOP was expected to decrease with torrefaction severity. A decrease in the proportion of oxygen-containing aliphatic compounds could improve the stability of the HOP [27,68]. Besides, the high ash content of SS torrefied at 320 °C and 6.1 min (38% higher compared to dry SS) could cause the degradation of oxygen-containing aliphatic compounds and therefore the decrease in the proportion of these compounds [62,67]. As mentioned before, the loss of extractive compounds during torrefaction decreases the proportion of steroids and their derivatives in pyrolysis liquid. The proportion of oxygen and nitrogen-containing aliphatic compounds and of oxygen and/or nitrogen-containing aromatic compounds in the HOP from TSS at 320 °C and 6.1 min is higher than that from pyrolysis of dry SS. Phenolic compounds such as phenol and cresols are abundant in the HOP and could come from the pyrolysis of polysaccharides and proteins [69]. It seems that the proportion of these compounds increases with torrefaction severity within the ranges of study. Most of both nitrogen-containing aliphatic and aromatic compounds come from the decomposition of proteins present in dry SS [70,71]. The proportion of nitrogen-containing compounds in the HOP such as nitriles increases with torrefaction severity because proteins barely react at temperatures below 300 °C but suffer cracking at temperatures between 300 °C and 500 °C [72].

3.4.3. AP

According to the results obtained, the yield of the AP and the yield of $\text{NH}_3\text{-N}$ are affected by the different torrefaction conditions but not its water content (Table 5).

3.4.3.1. AP yield. The yield of the pyrolysis aqueous phase ranges from $6 \pm 3\%$ to $22 \pm 3\%$ in the intervals of the torrefaction operational conditions under study (Fig. 8a). The yield of AP decreases

Table 6

Organic compounds identified in the LOP, HOP and AP from pyrolysis of dry SS, TSS obtained at 200 °C and 10.2 min and TSS obtained at 320 °C and 6.1 min (area percentage of the organic compound >1%). The organic compounds have been grouped by chemical families.

LOP	HOP	AP
Aliphatic compounds with oxygen		
(15E)-15-Heptadecenal ^{a,b}	(4E)-4-Methyl-6-(tetrahydro-2H-pyran-2-yloxy)-4-hexenal ^{b,c}	Acetic acid
1-Icosanol ^c	Dodecanoic acid ^{b,c}	Propionic acid
2,2-Dimethyl-3-[(3E,7E,11E,15E)-3,7,12,16,20-pentamethyl-3,7,11,15,19-henicosapentaen-1-yl]oxirane ^{b,c}	Myristic acid	2-Methylpropanoic acid
Methyl 4-acetoxy-1b-hydroxy-3-isopropenyl-5a-methyl-5-oxooctahydrospiro[indeno[1,2-b]oxirene-6,2'-oxirane]-2-carboxylate ^{a,b}	Pentadecanoic acid	Butyric acid
2,3-Dihydroxypropyl (9Z,12Z,15Z)-9,12,15-octadecatrienoate ^{b,c}	1-Hexadecanol	3-Methylbutanoic acid
	Palmitic acid	4-Methylpentanoic acid
	9-Hexadecenoic acid ^c	Hexanoic acid
	(9E)-9-Octadecenoic acid ^b	
	1-Octadecanol ^c	
	(9Z)-9-Octadecenoic acid	
	Stearic acid ^a	
	(11E)-11-Octadecenoic acid	
Aliphatic compounds with nitrogen		
Pentadecanenitrile ^c	Ethylamine ^{b,c}	Acetonitrile
Heptadecanenitrile	Hexadecanenitrile	
	Heptadecanenitrile ^{a,b}	
Aliphatic compounds with oxygen and nitrogen		
Formamide, N-[4-[2-(1,1-dimethylethyl)-5-oxo-1,3-dioxolan-4-yl]butyl] ^{b,c}	Norvaline ^{b,c}	Ethanimidic acid
9-Octadecenamide	D-Alanine	Propanimidic acid
	2-Aminoethanol ^{a,b}	2-Pyrrolidinone
	5,5-Dimethyl-2,4-imidazolidinedione	2-Piperidinone
	5,6-Dihydro-2,4-pyrimidinediol ^c	5,5-Dimethyl-2,4-imidazolidinedione
	2,4,5-Imidazolidinetrione ^{a,c}	1-Methyl-2-azepanone ^{b,c}
		Succinamide ^{b,c}
		5-Ethyl-5-methyl-2,4-imidazolidinedione
		5-Methyl-2,4-imidazolidinedione
		5-Isopropyl-2,4-imidazolidinedione
		3-Isobutylhexahydropyrrolo[1,2-a]pyrazine-1,4-dione
		(5S)-5-Isobutyl-2,4-imidazolidinedione ^{b,c}
Aromatic compounds with oxygen and/or nitrogen		
p-Cresol	Phenol	Benzoic acid
	o-Cresol	
	p-Cresol	
	m-Cresol	
	2,4-Dimethylphenol ^{a,c}	
	3,5-Dimethylphenol	
	4-Hydroxybenzaldehyde	
	Phenylacetonitrile	
	Hydroquinone	
	2-Methyl-3-[4-(2-methyl-2-propanyl)phenyl]propanal ^{b,c}	
	(4Z)-4-[(4-Methylphenyl)imino]-2-pentanone ^{a,b}	
	2,3-Dimethyl-2,3-diphenylsuccinonitrile ^{a,b}	
	1-Methyl-3,3-bis(2-methyl-2-propanyl)-1,3-dihydro-2H-indol-2-one ^{a,b}	
	3-Hydroxyphenylalanine	
Heterocyclic aromatic compounds (O and/or N)		
7-methyl-1H-indole ^{a,b}	4-(4-Methylphenyl)pyridine ^{a,b}	3-Pyridinamine
	1H-Imidazo[4,5-d]pyridazine ^{a,b}	3-Pyridinol
	1H-Indole ^c	2-Pyridinol
Aliphatic hydrocarbons		
1,3,5,7-Cyclooctatetraene ^{b,c}	1,3,5,7-Cyclooctatetraene	
1-Tetradecene ^{a,c}		
3-Tetradecene ^{a,b}		
1-Pentadecene ^a		
1-Hexadecene		
Octadecane ^a		

Table 6 (continued)

LOP	HOP	AP
Steroids and derivatives		
(3 β)-Cholest-5-en-3-ol	Cholest-4-ene ^b	
Cholesta-3,5-diene	Cholest-2-ene	
4-Methylcholesta-8,24-dien-3-ol	(5 β)-Cholest-3-ene	
Chol-8(14)-en-24-ol ^a	(3 β ,5 α)-Cholestan-3-ol ^{b,c}	
14-Methylcholest-8-en-3-one ^b	4-Methylcholesta-8,24-dien-3-ol	
(3 β ,4 α ,5 α)-4,14-Dimethylergosta-8,24(28)-dien-3-ol ^{a,b}		
(3 β)-Cholesta-5,7-dien-3-ol		
14-Methylcholest-8-en-3-one ^b		
Cholest-4-ene-3,6-dione ^{a,c}		
(3 β ,5 β ,15 β)-3-Hydroxy-14,15-epoxybua-20,22-dienolide		
(3 α ,5 β ,7 β ,8 ξ)-3,7-Dihydroxycholan-24-oic acid		
(3 β ,5 β ,15 β ,16 β)-3,16-Dihydroxy-14,15-epoxybua-20,22-dienolide ^c		
Stigmastan-3,5-diene ^c		
(3 β ,22E)-Ergosta-4,6,22-trien-3-ol ^{a,b}		
(5 α)-Cholestan-3-one ^{a,c}		
(5 α)-Cholest-3-ene		
(5 β)-Cholest-2-ene ^a		
Cholest-4-ene		
(5 α)-Cholest-2-ene ^b		
Cholest-1-ene ^c		
Cholest-2-ene		
Cholesta-2,4-diene		
Compounds with sulfur		
	1-[4-(Methylsulfanyl)phenyl]ethanone ^{a,b}	2-[(2-Methyl-2-propenyl)oxy]thiophene ^{a,c}

^a Not present when dry SS is pyrolyzed.

^b Not present when TSS obtained at 220 °C and 10.2 min is pyrolyzed.

^c Not present when TSS obtained at 320 °C and 6.1 min is pyrolyzed.

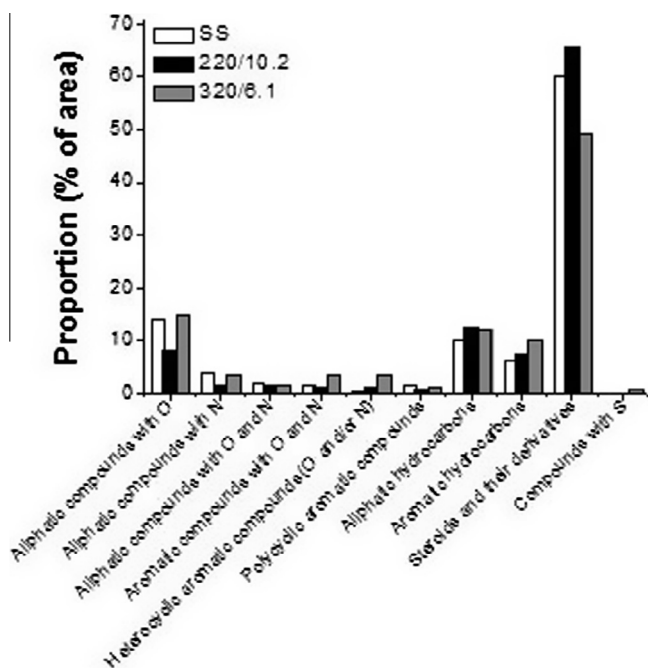


Fig. 6. Percentage of the different chemical families present in the LOP (% of area).

with the increasing torrefaction temperature from 270 °C to 320 °C at solid residence times longer than 6.1 min. At the highest torrefaction temperatures, the amount of water removed is higher because sewage sludge loses water by moisture evaporation but also by dehydration reactions. Therefore, it is logical that the AP yield decreases at the higher torrefaction temperatures. The AP yield is not affected by the torrefaction solid residence time within the range of temperatures studied.

Torrefaction decreases the yield of pyrolysis AP in almost all cases (Fig. 8b). Sewage sludge torrefied at 320 °C gives rise to the

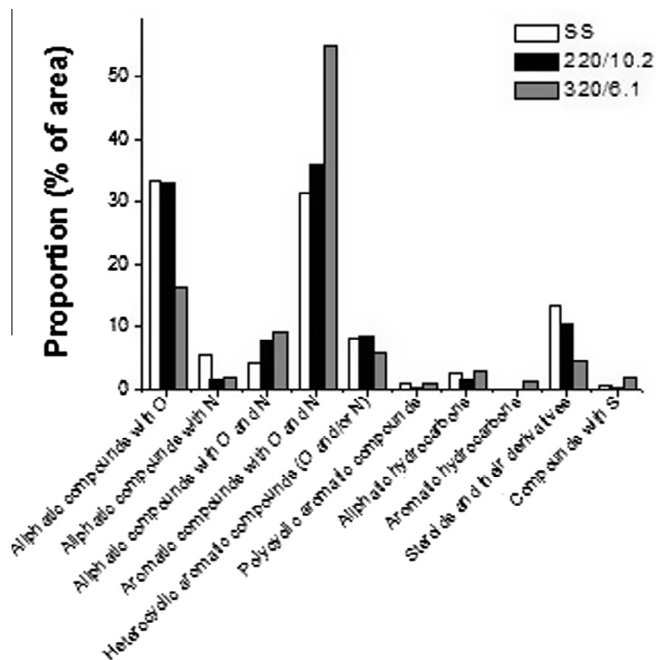


Fig. 7. Percentage of the different chemical families present in the HOP (% of area).

biggest reduction in AP yield compared to dry SS pyrolysis, namely an AP yield reduction between 43% and 83%. Comparing Fig. 8b with Fig. 3b it seems quite clear that the water yield strongly depends on the yield of the aqueous phase. The lower the AP yield, the lower the water yield.

3.4.3.2. NH_3 -N yield. The yield of NH_3 -N (present in the aqueous phase) obtained from pyrolysis of TSS experiments is affected by the different operational conditions used in torrefaction (see

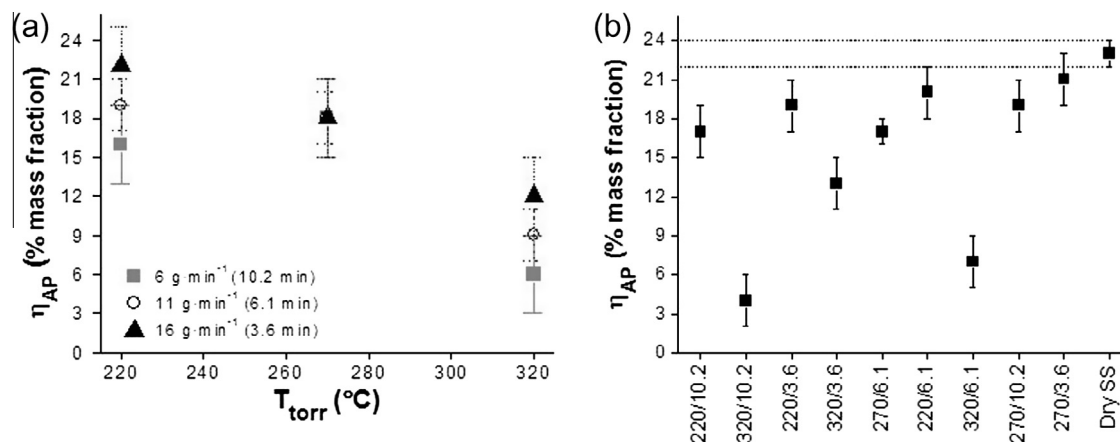


Fig. 8. (a) AP yield vs. torrefaction temperature for different torrefaction solid feed rate values. The results are expressed as the model value at each torrefaction condition ± 0.5 -Fisher LSD interval (taking into account all the runs). (b) Comparison of SS pyrolysis AP yield and TSS pyrolysis AP yield (LSD interval).

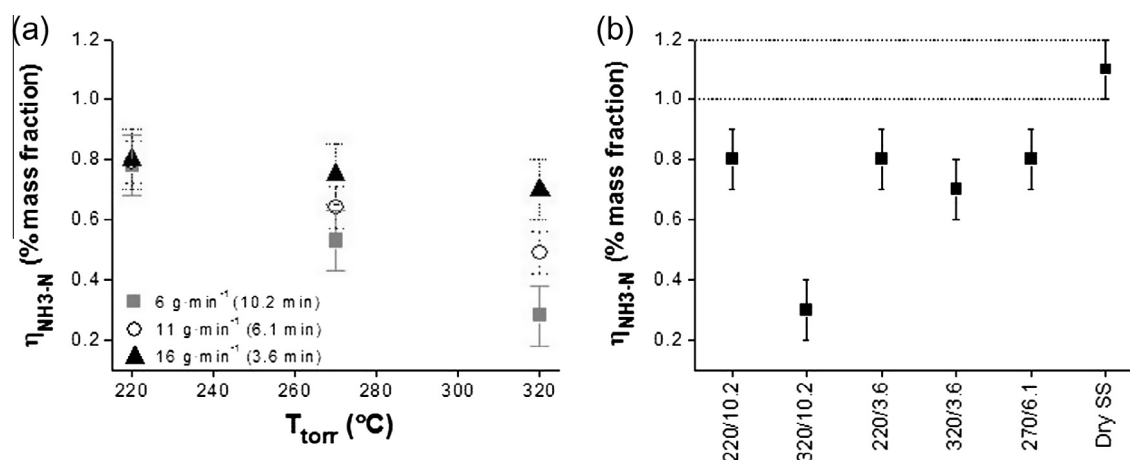


Fig. 9. (a) NH_3 -N yield vs. torrefaction temperature for different torrefaction solid feed rate values. The results are expressed as the model value at each torrefaction condition ± 0.5 -Fisher LSD interval (taking into account all the runs). (b) Comparison of SS pyrolysis NH_3 -N yield and TSS pyrolysis NH_3 -N yield (LSD interval).

Fig. 9a). At solid residence times of 6.1 min and 10.2 min, the yield of NH_3 -N decreases when the torrefaction temperature increases within the range of study. At torrefaction temperatures of 270 °C and 320 °C the yield of NH_3 -N from TSS obtained at solid residence time of 3.6 min is higher than from TSS obtained at 10.2 min.

It can be observed in **Fig. 9b** that the yield of NH_3 -N obtained when pyrolysis of dry SS is carried out is significantly higher than those values from pyrolysis of TSS. Moreover, the experiment carried out at the most severe torrefaction operational conditions (320 °C and 10.2 min) gives the lowest yield of this compound. This fact could be due to the removal of NH_3 -N during the torrefaction step when it is conducted at high enough temperatures (320 °C) and long enough solid residence times (10.2 min). At these torrefaction operational conditions, the proteins or their fractions present in SS, which contain an amino group, could begin to suffer cracking reactions [72], yielding NH_3 -N.

3.4.3.3. Chemical composition of the AP. The organic compounds identified in the AP obtained from pyrolysis of dry SS, TSS at 220 °C and 10.2 min and TSS at 320 °C and 6.1 min have been grouped into chemical families. The area percentage of each of the chemical families identified is shown in **Fig. 10**. The proportion of the different families present in the AP from pyrolysis of TSS does not change substantially compared to the AP from pyrolysis of dry SS. As can be observed in **Table 6**, the organic compounds with area percentage larger than 1% are practically the same in

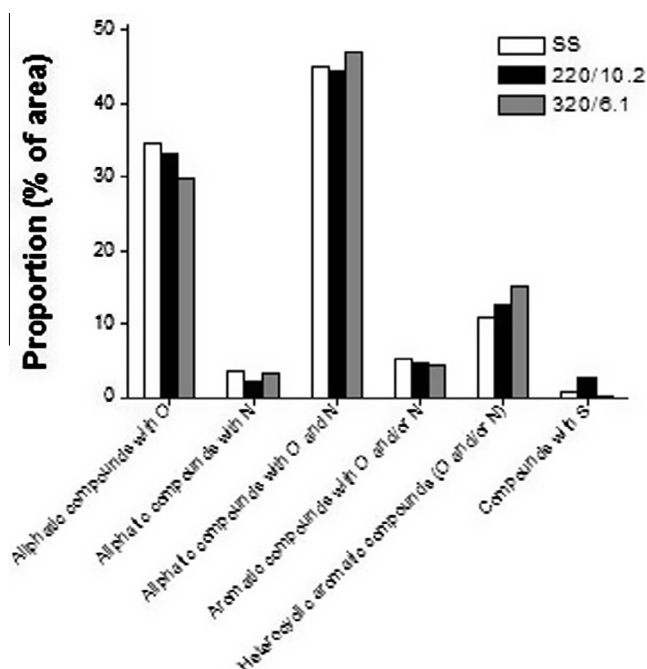


Fig. 10. Percentage of the different chemical families present in the AP (% of area).

the three AP analyzed. Oxygen-containing aliphatic compounds (mainly fatty acids) and oxygen and nitrogen-containing aliphatic compounds such as amides and diimides are the major compounds. It seems that the proportion of oxygen-containing aliphatic compounds in pyrolysis AP slightly decreases with torrefaction severity. Acetic acid is one of the main compounds in these phases, possibly arising from the acetoxy- and methoxy-groups present in hemicellulose [53,73]. The proportion of oxygen and/or nitrogen-containing heterocyclic aromatic compounds such as pyridinols mildly increases with torrefaction severity. The nitrogen-containing compounds, which give these phases their basic character, could come from the cracking of the proteins present in the SS.

4. Conclusions

The influence of sewage sludge pre-treatment by means of torrefaction on the distribution and properties of pyrolysis products has been investigated.

Torrefaction pre-treatment does not affect either char yield or NCG yield, but under severe enough torrefaction conditions torrefaction pre-treatment decreases the yield of water and organic compounds from pyrolysis.

No differences are found between the cumulative liquid, NCG, and organic yields of the processes carried out in two steps and the yield from pyrolysis of dry sewage sludge under the operation conditions studied in the present work.

Torrefaction pre-treatment does not improve the homogeneity of the liquid. Despite the reduction in the liquid water content, the three phases continue to appear. The pre-treatment decreases the yield of the light organic phase and especially the yield of the aqueous phase, although the water content of the latter does not change. Neither the water content of the HOP is reduced by the torrefaction pretreatment in this work. The higher heating value of the organic phases is not affected by torrefaction within the ranges of study.

Although the AP chemical composition is barely affected by the pretreatment, the chemical composition of the organic phases (LOP and HOP) is modified by torrefaction. It is remarkable that when sewage sludge torrefied under severe conditions is pyrolyzed, the proportion of oxygen-containing aliphatic hydrocarbons in the HOP decreases.

Therefore, although torrefaction of dry SS under the conditions tested in this study does not provoke any noticeable benefit in the improvement of pyrolysis liquid fuel properties, given the decrease in the proportion of oxygen-containing aliphatic compounds it would be interesting to try longer torrefaction solid residence times, since it seems that this pre-treatment could enhance the stability of the liquid.

Acknowledgment

The authors would like to express their gratitude to the Spanish Ministry of Science and Innovation for financial support for this work (CTQ2010-20137PPQ).

References

- [1] H.B. Goyal, D. Seal, R.C. Saxena, Bio-fuels from thermochemical conversion of renewable resources: a review, *Renew. Sustain. Energy Rev.* 12 (2008) 504–517.
- [2] P. Tanger, J.L. Field, C.E. Jahn, M.W. Defoort, J.E. Leach, Biomass for thermochemical conversion: targets and challenges, *Front. Plant Sci.* 4 (2013), pp. 218–218.
- [3] C. Briens, J. Piskorz, F. Berruti, Biomass valorization for fuel and chemicals production – a review, *Int. J. Chem. React. Eng.* 6 (2008).
- [4] A.V. Bridgwater, Principles and practice of biomass fast pyrolysis processes for liquids, *J. Anal. Appl. Pyrol.* 51 (1999) 3–22.
- [5] I. Fonts, G. Gea, M. Azuara, J. Ábrego, J. Arauzo, Sewage sludge pyrolysis for liquid production: a review, *Renew. Sustain. Energy Rev.* 16 (2012) 2781–2805.
- [6] Y. Cao, A. Pawłowski, Sewage sludge-to-energy approaches based on anaerobic digestion and pyrolysis: brief overview and energy efficiency assessment, *Renew. Sustain. Energy Rev.* 16 (2012) 1657–1665.
- [7] Y. Kim, W. Parker, A technical and economic evaluation of the pyrolysis of sewage sludge for the production of bio-oil, *Bioresour. Technol.* 99 (2008) 1409–1416.
- [8] Q. Zhang, J. Chang, T. Wang, Y. Xu, Review of biomass pyrolysis oil properties and upgrading research, *Energy Convers. Manage.* 48 (2007) 87–92.
- [9] I. Fonts, A. Juan, G. Gea, M.B. Murillo, J. Arauzo, Sewage sludge pyrolysis in a fluidized bed, 2: influence of operating conditions on some physicochemical properties of the liquid product, *Ind. Eng. Chem. Res.* 48 (2009) 2179–2187.
- [10] M. Inguaño, A. Domínguez, J.A. Menéndez, C.G. Blanco, J.J. Pis, On the pyrolysis of sewage sludge: the influence of pyrolysis conditions on solid, liquid and gas fractions, *J. Anal. Appl. Pyrol.* 63 (2002) 209–222.
- [11] E. Pokorna, N. Postelmans, P. Jenicek, S. Schreurs, R. Carleer, J. Yperman, Study of bio-oils and solids from flash pyrolysis of sewage sludges, *Fuel* 88 (2009) 1344–1350.
- [12] I. Fonts, E. Kuoppala, A. Oasmaa, Physicochemical properties of product liquid from pyrolysis of sewage sludge, *Energy Fuels* 23 (2009) 4121–4128.
- [13] J. Piskorz, D.S. Scott, I.B. Westerberg, Flash pyrolysis of sewage-sludge, *Ind. Eng. Chem. Process Des. Dev.* 25 (1986) 265–270.
- [14] M.E. Sánchez, J.A. Menéndez, A. Domínguez, J.J. Pis, O. Martínez, L.F. Calvo, P.L. Bernad, Effect of pyrolysis temperature on the composition of the oils obtained from sewage sludge, *Biomass Bioenergy* 33 (2009) 933–940.
- [15] Q. Lu, W.Z. Li, X.F. Zhu, Overview of fuel properties of biomass fast pyrolysis oils, *Energy Convers. Manage.* 50 (2009) 1376–1383.
- [16] J.P. Diebold, A review of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-oils, in: A.V. Bridgwater (Ed.), *Fast Pyrolysis of Biomass: A handbook*, CPL Press, Newbury, U.K., 2002, pp. 205–241.
- [17] Q. Lu, Z.-F. Zhang, C.-Q. Dong, X.-F. Zhu, Catalytic upgrading of biomass fast pyrolysis vapors with nano metal oxides: an analytical Py-GC/MS study, *Energies* 3 (2010) 1805–1820.
- [18] Q. Lu, X. Zhu, W. Li, Y. Zhang, D. Chen, On-line catalytic upgrading of biomass fast pyrolysis products, *Chin. Sci. Bull.* 54 (2009) 1941–1948.
- [19] R. French, S. Czernik, Catalytic pyrolysis of biomass for biofuels production, *Fuel Process. Technol.* 91 (2009) 25–32.
- [20] M. Azuara, I. Fonts, P. Barcelona, M.B. Murillo, G. Gea, Study of catalytic post-treatment of the vapours from sewage sludge pyrolysis by means of gamma-Al₂O₃, *Fuel* 107 (2013) 113–121.
- [21] S. Thangalazhy-Gopakumar, S. Adhikari, R.B. Gupta, M. Tu, S. Taylor, Production of hydrocarbon fuels from biomass using catalytic pyrolysis under helium and hydrogen environments, *Bioresour. Technol.* 102 (2011) 6742–6749.
- [22] C. Torri, I.G. Lesci, D. Fabbri, Analytical study on the pyrolytic behaviour of cellulose in the presence of MCM-41 mesoporous materials, *J. Anal. Appl. Pyrol.* 85 (2009) 192–196.
- [23] H. Zhang, R. Xiao, D. Wang, Z. Zhong, M. Song, Q. Pan, G. He, Catalytic fast pyrolysis of biomass in a fluidized bed with fresh and spent fluidized catalytic cracking (FCC) catalysts, *Energy Fuels* 23 (2009) 6199–6206.
- [24] T.V. Choudhary, C.B. Phillips, Renewable fuels via catalytic hydrodeoxygenation, *Appl. Catal. A Gen.* 397 (2011) 1–12.
- [25] N. Joshi, A. Lawal, Hydrodeoxygenation of pyrolysis oil in a microreactor, *Chem. Eng. Sci.* 74 (2012) 1–8.
- [26] S.R.A. Kersten, W.P.M. van Swaaij, L. Lefferts, K. Sessa, Options for Catalysis in the Thermochemical Conversion of Biomass into Fuels, in: G. Centi, R.A. van Santen (Eds.), *Catalysis for Renewables: From Feedstock to Energy Production*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2007, pp. 119–146.
- [27] A.V. Bridgwater, Review of fast pyrolysis of biomass and product upgrading, *Biomass Bioenergy* 38 (2012) 68–94.
- [28] A. Atutxa, R. Aguado, A.G. Gayubo, M. Olazar, J. Bilbao, Kinetic description of the catalytic pyrolysis of biomass in a conical spouted bed reactor, *Energy Fuels* 19 (2005) 765–774.
- [29] A.A. Lappas, M.C. Samolada, D.K. Iatridis, S.S. Voutetakis, I.A. Vasalos, Biomass pyrolysis in a circulating fluid bed reactor for the production of fuels and chemicals, *Fuel* 81 (2002) 2087–2095.
- [30] D.C. Elliott, Historical developments in hydroprocessing bio-oils, *Energy Fuels* 21 (2007) 1792–1815.
- [31] P. Grange, E. Laurent, R. Maggi, A. Centeno, B. Delmon, Hydrotreatment of pyrolysis oils from biomass: reactivity of the various categories of oxygenated compounds and preliminary techno-economical study, *Catal. Today* 29 (1996) 297–301.
- [32] M. Ikura, M. Stanculescu, E. Hogan, Emulsification of pyrolysis derived bio-oil in diesel fuel, *Biomass Bioenergy* 24 (2003) 221–232.
- [33] X. Jiang, N. Ellis, Upgrading bio-oil through emulsification with biodiesel: thermal stability, *Energy Fuels* 24 (2010) 2699–2706.
- [34] J.M. Xu, J.C. Jiang, W.D. Dai, T.J. Zhang, Y. Xu, Bio-oil upgrading by means of ozone oxidation and esterification to remove water and to improve fuel characteristics, *Energy Fuels* 25 (2011) 1798–1801.
- [35] N. Lohitharn, B.H. Shanks, Upgrading of bio-oil: effect of light aldehydes on acetic acid removal via esterification, *Catal. Commun.* 11 (2009) 96–99.
- [36] V.A. Doshi, H.B. Vuthaluru, T. Bastow, Investigations into the control of odour and viscosity of biomass oil derived from pyrolysis of sewage sludge, *Fuel Process. Technol.* 86 (2005) 885–897.

- [37] J. Meng, J. Park, D. Tilotta, S. Park, The effect of torrefaction on the chemistry of fast-pyrolysis bio-oil, *Bioresour. Technol.* 111 (2012) 439–446.
- [38] B.-I. Na, Y.-H. Kim, W.-S. Lim, S.-M. Lee, H.-W. Lee, J.-W. Lee, Torrefaction of oil palm mesocarp fiber and their effect on pelletizing, *Biomass Bioenergy* 52 (2013) 159–165.
- [39] M. Atienza-Martínez, I. Fonts, J. Ábrego, J. Ceamanos, G. Gea, Sewage sludge torrefaction in a fluidized bed reactor, *Chem. Eng. J.* 222 (2013) 534–545.
- [40] M.J.C. van der Stelt, H. Gerhauser, J.H.A. Kiel, K.J. Ptasiński, Biomass upgrading by torrefaction for the production of biofuels: a review, *Biomass Bioenergy* 35 (2011) 3748–3762.
- [41] P. Rousset, C. Aguiar, N. Labbe, J.M. Commandre, Enhancing the combustible properties of bamboo by torrefaction, *Bioresour. Technol.* 102 (2011) 8225–8231.
- [42] M.J. Prins, K.J. Ptasiński, F. Janssen, Torrefaction of wood – Part 1. Weight loss kinetics, *J. Anal. Appl. Pyrol.* 77 (2006) 28–34.
- [43] T.G. Bridgeman, J.M. Jones, I. Shield, P.T. Williams, Torrefaction of reed canary grass, wheat straw and willow to enhance solid fuel qualities and combustion properties, *Fuel* 87 (2008) 844–856.
- [44] M. Phanphanich, S. Mani, Impact of torrefaction on the grindability and fuel characteristics of forest biomass, *Bioresour. Technol.* 102 (2010) 1246–1253.
- [45] J.M. Jones, T.G. Bridgeman, L.I. Darvell, B. Gudka, A. Saddawi, A. Williams, Combustion properties of torrefied willow compared with bituminous coals, *Fuel Process. Technol.* 101 (2012) 1–9.
- [46] C. Couhert, S. Salvador, J.M. Commandre, Impact of torrefaction on syngas production from wood, *Fuel* 88 (2009) 2286–2290.
- [47] M.J. Prins, K.J. Ptasiński, F. Janssen, More efficient biomass gasification via torrefaction, *Energy* 31 (2006) 3458–3470.
- [48] Q. Chen, J.S. Zhou, B.J. Liu, Q.F. Mei, Z.Y. Luo, Influence of torrefaction pretreatment on biomass gasification technology, *Chin. Sci. Bull.* 56 (2011) 1449–1456.
- [49] J. Deng, G.-J. Wang, J.-H. Kuang, Y.-L. Zhang, Y.-H. Luo, Pretreatment of agricultural residues for co-gasification via torrefaction, *J. Anal. Appl. Pyrol.* 86 (2009) 331–337.
- [50] A. Zheng, Z. Zhao, S. Chang, Z. Huang, F. He, H. Li, Effect of torrefaction temperature on product distribution from two-staged pyrolysis of biomass, *Energy Fuels* 26 (2012) 2968–2974.
- [51] A. Zheng, Z. Zhao, S. Chang, Z. Huang, X. Wang, F. He, H. Li, Effect of torrefaction on structure and fast pyrolysis behavior of corncobs, *Bioresour. Technol.* 128 (2013) 370–377.
- [52] R.J.M. Westerhof, D.W.F. Brilman, M. Garcia-Perez, Z. Wang, S.R.G. Oudenhoven, S.R.A. Kersten, Stepwise fast pyrolysis of pine wood, *Energy Fuels* 26 (2012) 7263–7273.
- [53] S.-S. Liaw, S. Zhou, H. Wu, M. Garcia-Perez, Effect of pretreatment temperature on the yield and properties of bio-oils obtained from the auger pyrolysis of Douglas fir wood, *Fuel* 103 (2013) 672–682.
- [54] J.N. Murwanashyaka, H. Pakdel, C. Roy, Step-wise and one-step vacuum pyrolysis of birch-derived biomass to monitor the evolution of phenols, *J. Anal. Appl. Pyrol.* 60 (2001) 219–231.
- [55] A.A. Boateng, C.A. Mullen, Fast pyrolysis of biomass thermally pretreated by torrefaction, *J. Anal. Appl. Pyrol.* 100 (2013) 95–102.
- [56] S. Ren, H. Lei, L. Wang, Q. Bu, S. Chen, J. Wu, J. Julson, R. Ruan, The effects of torrefaction on compositions of bio-oil and syngas from biomass pyrolysis by microwave heating, *Bioresour. Technol.* 135 (2013) 659–664.
- [57] M. Atienza-Martínez, G. Gea, J. Arauzo, S.R.A. Kersten, A.M.J. Kootstra, Phosphorus recovery from sewage sludge char ash, *Biomass Bioenergy* 65 (2014) 42–50.
- [58] I. Fonts, A. Juan, G. Gea, M.B. Murillo, J.L. Sanchez, Sewage sludge pyrolysis in fluidized bed, 1: influence of operational conditions on the product distribution, *Ind. Eng. Chem. Res.* 47 (2008) 5376–5385.
- [59] A.D. Eaton, L.S. Clescer, A.E. Greenberg, Standard Methods for the Examination of Water and Wastewater, American Public Health Association, American Water Works, Water Environment Federation, Hanover, MD, 1995.
- [60] D.C. Montgomery, Design and Analysis of Experiments, Fifth ed., Wiley, New York, 2001.
- [61] N. Gil-Lalaguna, I. Fonts, G. Gea, M.B. Murillo, L. Lazaro, Reduction of water content in sewage sludge pyrolysis liquid by selective online condensation of the vapors, *Energy Fuels* 24 (2010) 6555–6564.
- [62] I. Fonts, M. Azuara, L. Lazaro, G. Gea, M.B. Murillo, Gas chromatography study of sewage sludge pyrolysis liquids obtained at different operational conditions in a fluidized bed, *Ind. Eng. Chem. Res.* 48 (2009) 5907–5915.
- [63] C. Jindarom, V. Meeyoo, T. Rirkomboon, P. Rangsunvigit, Thermochemical decomposition of sewage sludge CO₂ and N₂ atmosphere, *Chemosphere* 67 (2007) 1477–1484.
- [64] D.G.B. Boocock, S.K. Konar, A. Mackay, P.T.C. Cheung, J. Liu, Fuels and chemical from sewage-sludge 2. The production of alkanes and alkenes by the pyrolysis of triglycerides over activated alumina, *Fuel* 71 (1992) 1291–1297.
- [65] K.D. Maher, D.C. Bressler, Pyrolysis of triglyceride materials for the production of renewable fuels and chemicals, *Bioresour. Technol.* 98 (2007) 2351–2368.
- [66] P.F. Britt, A.C. Buchanan III, M.K. Kidder, C.V. Owens (Jr.), Influence of steroid structure on the pyrolytic formation of polycyclic aromatic hydrocarbons, *J. Anal. Appl. Pyrol.* 66 (2003) 71–95.
- [67] I. Fonts, M. Azuara, G. Gea, M.B. Murillo, Study of the pyrolysis liquids obtained from different sewage sludge, *J. Anal. Appl. Pyrol.* 85 (2009) 184–191.
- [68] S. Czernik, A.V. Bridgwater, Overview of applications of biomass fast pyrolysis oil, *Energy Fuels* 18 (2004) 590–598.
- [69] V. Parnaudeau, M.-F. Dignac, The organic matter composition of various wastewater sludges and their neutral detergent fractions as revealed by pyrolysis-GC/MS, *J. Anal. Appl. Pyrol.* 78 (2007) 140–152.
- [70] J.-P. Cao, L.-Y. Li, K. Morishita, X.-B. Xiao, X.-Y. Zhao, X.-Y. Wei, T. Takarada, Nitrogen transformations during fast pyrolysis of sewage sludge, *Fuel* 104 (2010) 1–6.
- [71] J.-P. Cao, X.-Y. Zhao, K. Morishita, X.-Y. Wei, T. Takarada, Fractionation and identification of organic nitrogen species from bio-oil produced by fast pyrolysis of sewage sludge, *Bioresour. Technol.* 101 (2010) 7648–7652.
- [72] J. Zhang, Y. Tian, Y. Cui, W. Zuo, T. Tan, Key intermediates in nitrogen transformation during microwave pyrolysis of sewage sludge: a protein model compound study, *Bioresour. Technol.* 132 (2013) 57–63.
- [73] M.J. Prins, K.J. Ptasiński, F. Janssen, Torrefaction of wood – Part 2. Analysis of products, *J. Anal. Appl. Pyrol.* 77 (2006) 35–40.